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(12) **United States Patent**  
**Jadhav et al.**

(10) **Patent No.:** **US 7,473,685 B2**  
(45) **Date of Patent:** **Jan. 6, 2009**

(54) **PROCESS FOR PREPARATION OF CHEMICALLY STABLE, DRY-FLOW, LOW COMPACT, DUST FREE, SOLUBLE GRANULES OF PHOSPHOROAMIDOTHIOATES**

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(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(Continued)

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(21) Appl. No.: **11/060,283**

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(65) **Prior Publication Data**  
US 2005/0143351 A1 Jun. 30, 2005

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**Related U.S. Application Data**

(63) Continuation of application No. 10/126,965, filed on Apr. 22, 2002, now Pat. No. 6,875,381.

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(60) Provisional application No. 60/340,272, filed on Dec. 18, 2001.

(57) **ABSTRACT**

(51) **Int. Cl.**  
*A01N 57/02* (2006.01)

Dry flow, low compact, dust free, soluble granules of phosphoroamidothioates, preferably acephate, are produced by the process of 1) pre-mixing technical grade phosphoroamidothioate with specified adjuvants and other inert ingredients; 2) grinding to produce a ground product having a preferred particle size of 5 microns to 10 microns; 3) post-mixing; 4) granulating; 5) drying; 6) sizing to required length, preferably 1.5 to 3.0 mm; 7) and sieving to remove the fines to get the desired dust free soluble granule.

(52) **U.S. Cl.** ..... 514/120; 424/408; 424/409; 424/417; 424/421

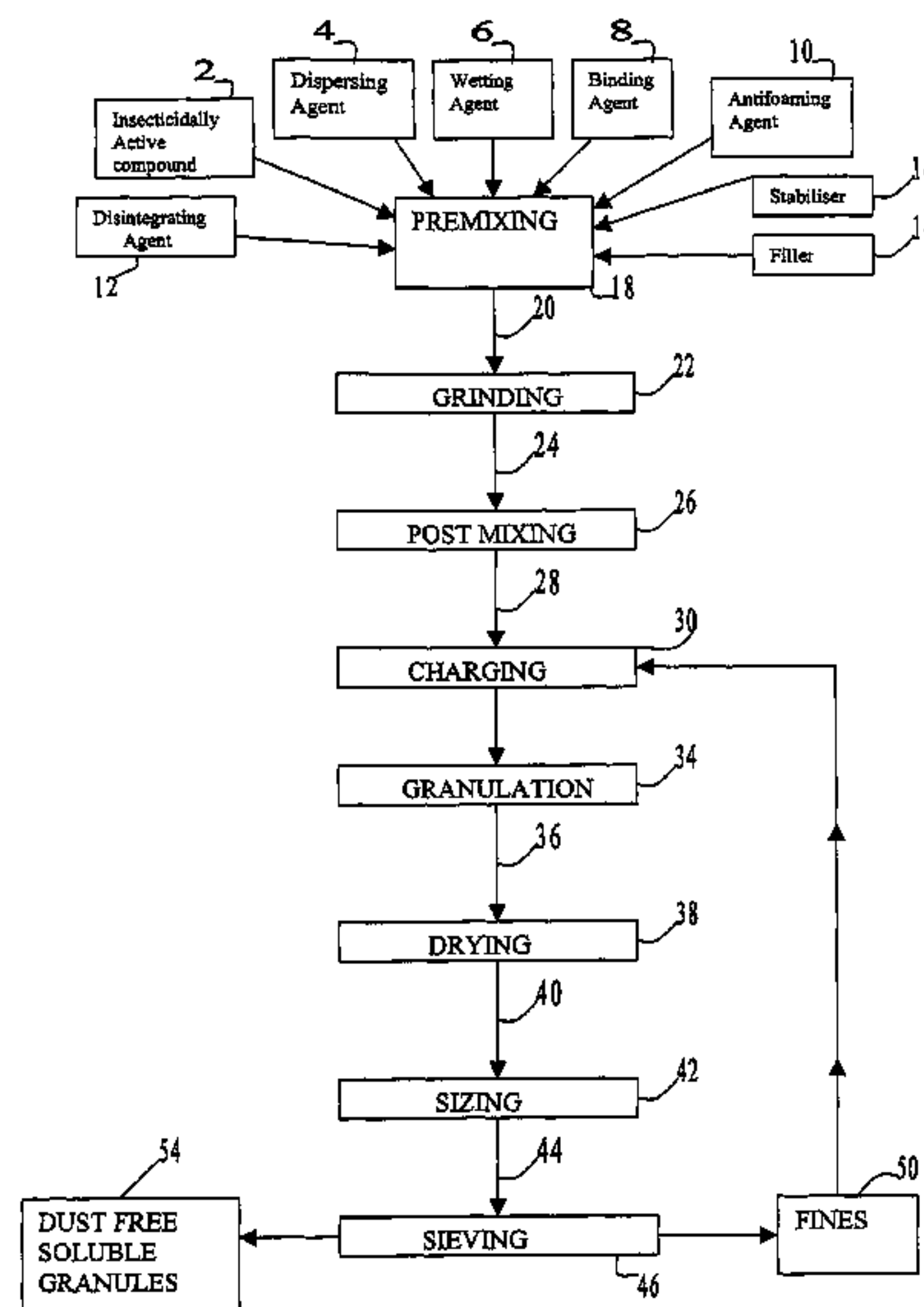
(58) **Field of Classification Search** ..... None  
See application file for complete search history.

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**12 Claims, 1 Drawing Sheet**



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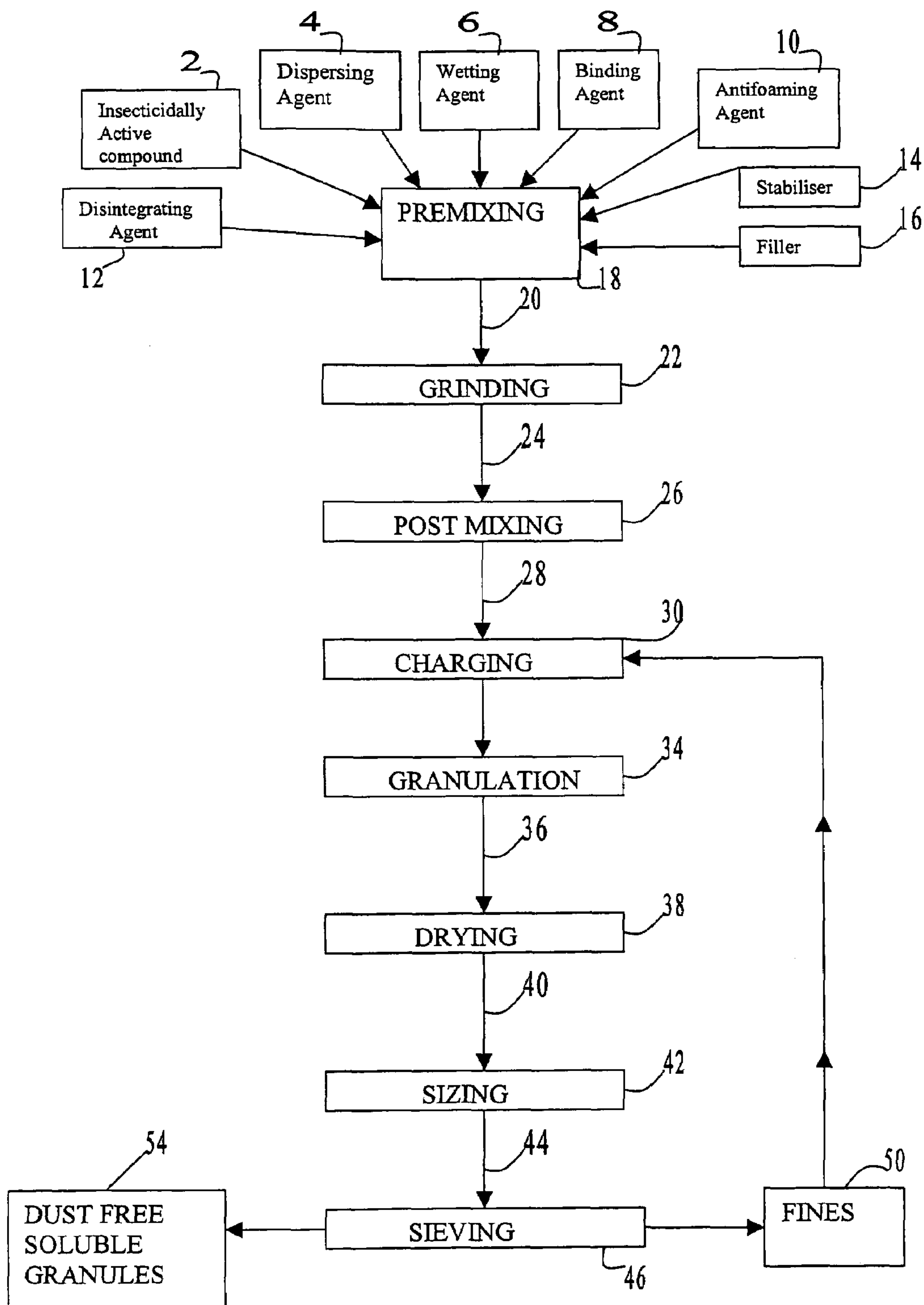


FIG. 1



**PROCESS FOR PREPARATION OF  
CHEMICALLY STABLE, DRY-FLOW, LOW  
COMPACT, DUST FREE, SOLUBLE  
GRANULES OF  
PHOSPHOROAMIDOTHIOATES**

CROSS REFERENCE TO RELATED  
APPLICATION

This application claims the benefit, under 35 U.S.C. 119 (e), of U.S. Provisional Application No. 60/340,272 filed Dec. 18, 2001, the contents of which are incorporated herein by reference.

This application is a continuation application of U.S. Ser. No. 10/126,965 filed Apr. 22, 2002 now U.S. Pat. No. 6,875,381, the contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for preparing insecticidally active soluble granules of phosphoroamidothioate, referred to herein as acephate.

2. Background Information

In recent years, agricultural chemicals have been most preferably formulated in the form of dusts, wettable powders, soluble powders, emulsifiable concentrates, soluble liquid/concentrates, granules, coated granules, water dispersible granules, suspension concentrates, and solutions. Occasionally, when dusts are produced by absorbing or mixing active ingredients with a finely divided inert carrier material, for example China Clay or the like, drift problems occur. With wettable powders and soluble powders the problems faced at the time of dilution are not only drift, but the final disposal of containers, for dust particles tend to stick to sides of the containers. The left over materials within the containers pose great problems to the environment, operators and users.

Although dusts are undesirable because of airborne contamination and handling difficulties, liquid spray formulations have not provided an acceptable alternative, for they involve solvents and packaging expenses, along with container disposal requirements that detract from their commercial desirability.

Water dispersible granules produced by fluidized bed spray dryers overcome the problems associated with wettable powders and soluble powders, but have high processing costs and require high value capital investment, as well as requiring highly skilled staff. These problems impose a significant barrier in widening the market acceptance of these compounds.

Certain phosphoroamidothioates and phosphoroamidodithioates, collectively referred to as Phosphoroamidothioates, are known to have excellent insecticidal activity against a variety of insects and in a variety of environments. Acephate, one of the important commercial insecticides within this class of compounds, is a systemic and contact insecticide of moderate persistence with residual activity lasting about 10-15 days. It is effective against a wide range of aphids, leaf-miners, lepidopterous, larvae, sawflies and thrips and it is also a non-phytotoxic on many crop plants.

Phosphoroamidothioate containing pellets have been proposed in the past, but difficulties have been encountered in pelletizing acephate technical, the preferred insecticide within the class of phosphoroamidothioates. Attempts to manufacture acephate technical pellets from acephate technical powders have been proposed and have been unsuccessful.

Considerable experimentation in the area of producing the preferred high-strength acephate granules has been conducted and confirms the manufacturing difficulties which earlier formulators have experienced. Furthermore, the pellets and methods proposed for making pellets suggested in the prior art leave considerable room for improvement. Prior extrusion processes have proposed the addition of costly surfactants, the combination of phosphoroamidothioate with a second active ingredient, or the creation of a mixture of the active ingredient with a solvent in an amount of from 3-25% by weight before extrusion, but these processes have not solved the problems encountered.

The formulation of acephate presently in use is acephate 75% soluble powder having acephate active ingredient 75% (w/w), surfactant 1 to 2% (w/w), inert filler (precipitated silica) to make 100% (w/w). Acephate 75% soluble powder poses the problems of dust, low pourability, high transportation costs, high capital manufacturing investment, measurement difficulties, difficulties in packing material disposal, handling problems, high risk of caking and others.

Because of the problems associated with producing granular forms of phosphoroamidothioates, such as the preferred acephate, there is a need in the art for a process for preparing chemically stable, dry flow, low compact, dust free, insecticidally active soluble granules of phosphoroamidothioate which are useful from a practical stand point, as well as for a low cost, practical manufacturing technique which can be practiced on a commercial scale without requiring expensive additives or solvents.

SUMMARY OF THE INVENTION

By the present invention the above-identified major limitations have been overcome. The method for producing dry flow, low-compact, dust free, soluble phosphoroamidothioate granules, such as the preferred compound acephate, is an improvement over prior manufacturing processes. Further, the dust free soluble granules produced by this invention, which has a concentration of the insecticidally active ingredient in this formulation may vary from 40-98% of phosphoroamidothioate active ingredient, is more advantageous than prior granular products and exhibits certain very desirable characteristics as noted hereinafter.

Briefly, and in accordance with a preferred embodiment of the invention, dry flow, low compact, dust free, soluble granules of insecticidally active phosphoroamidothioate are prepared by forming a pre-mix containing the required quantity of phosphoroamidothioate, a dispersing agent, a wetting agent, a binding agent, an antifoaming agent, a disintegrating agent, a stabilizer and filler. The specified adjuvants have a maximum of 1% water insoluble matter. This pre-mix is then ground to produce a ground product having preferred particle sizes between 5.0 microns to 10.0 microns. The ground product is fed to a post-mixer to form a mixture. The mixture is then fed through a hopper into a granulator where granules are formed. The granules are then dried, and the dried granules are sized and sieved to separate dry granules from fines, producing dry flow, low compact, dust free, soluble granules of phosphoroamidothioate as noted above, the preferred phosphoroamidothioate is acephate. The fines may be recycled back to the post mixer.

This invention produces essentially dry flow, low compact, dust free soluble phosphoroamidothioate granules having a preferred granule size of 1.5 to 3.0 mm in length and 0.5 to 1.0 mm in diameter. These granules of phosphoroamidothioates are characterized by aging stability for a minimum of two years.





**5**  
EXAMPLE 2

Acephate 98% granules can be prepared as follows:

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<u>Composition</u>	
Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	99.50
Dispersing agent	0.25
Wetting agent	0.03
Binding agent	0.05
Antifoaming agent	0.02
Disintegrating agent	0.05
Stabilizer	0.05
Filler	0.05
Total	100.00

Acephate 98% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 3

Acephate 97.5% granules can be prepared as follows:

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<u>Composition</u>	
Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	98.99
Dispersing agent	0.40
Wetting agent	0.10
Binding agent	0.10
Antifoaming agent	0.03
Disintegrating agent	0.20
Stabilizer	0.05
Filler	0.13
Total	100.00

Acephate 97.5% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 4

Acephate 90% Granules can be prepared as follows:

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<u>Composition</u>	
Ingredient	Quantity(% w/w)
Acephate Technical 98.5% purity	91.38
Dispersing agent	00.75
Wetting agent	00.10
Binding agent	00.20
Antifoaming agent	00.03
Disintegrating agent	01.00
Stabilizer	00.50
Filler	06.04
Total	100.00

Acephate 90% granules with above composition can be prepared by following the process described in EXAMPLE 1.

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EXAMPLE 5

Acephate 85% granules can be prepared as follows:

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<u>Composition</u>	
Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	86.30
Dispersing agent	01.50
Wetting agent	00.50
Binding agent	01.00
Antifoamer	00.05
Disintegrating agent	02.00
Stabilizer	00.60
Filler	08.05
Total	100.00

Acephate 85% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 6

Acephate 75% Granules can be prepared as follows:

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<u>Composition</u>	
Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	76.15
Dispersing agent	2.00
Wetting agent	1.50
Binding agent	1.50
Antifoaming agent	0.06
Disintegrating agent	5.00
Stabilizer	0.75
Filler	13.04
Total	100.00

Acephate 75% Granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 7

Acephate 50% Granules can be prepared as follows:

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<u>Composition</u>	
Ingredients	Quantity (% w/w)
Acephate Technical 98.5% purity	50.77
Dispersing agent	3.00
Wetting agent	2.00
Binding agent	3.00
Antifoaming agent	0.08
Disintegrating agent	10.00
Stabilizer	1.00
Filler	30.15
Total	100.00

Acephate 50% Granules with above composition can be prepared by following the process described in EXAMPLE 1.



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## EXAMPLE 8

Acephate 40% granules can be prepared as follows:

Composition	
Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	40.61
Dispersing agent	4.50
Wetting agent	3.00
Binding agent	3.00
Antifoaming agent	0.08
Disintegrating agent	12.00
Stabilizer	1.50
Filler	35.31
Total	100.00

Acephate 40% Granules of above composition can be prepared by following the process described in EXAMPLE 1.

## Tests

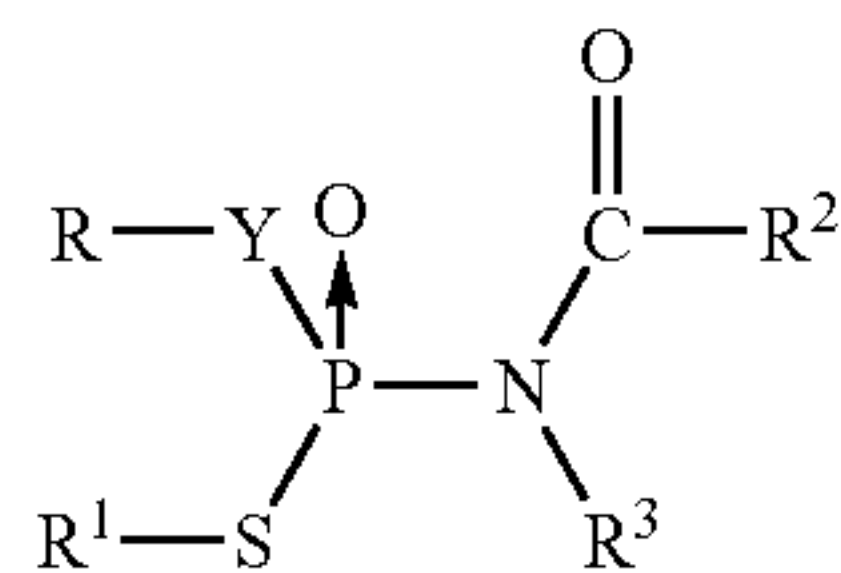
The physical properties of Acephate granules were determined before and after aging at 45° C. for 500 hrs and for flowability, wetting time, attrition test, disintegration rate, tap density, suspensibility, sedimentation and persistent foam. No noticeable difference in all the above properties was observed. The dynamic wetting time and solubility test was measured as per MT-167 of CIPAC. The flowability was measured as per MT-172 of CIPAC. The dry sieve analysis was measured as per MT-170 of CIPAC. The sedimentation was measured as per MT-15.1 of CIPAC. Dustiness of granules was measured as per MT-171 of CIPAC. The tap density was measured as per MT-58.4 and MT-33 of CIPAC. The Acephate technical was determined by the GLC method published in AOAC.

Although the present invention has been disclosed in terms of a preferred embodiment, it will be understood that numerous additional modifications and variations can be made without departing from the scope of the invention as defined by the following claims.

We claim:

1. A chemically stable dry flow, low compact, dust free soluble phosphoramidothioate granule consisting of

(i) 85-98% w/w an insecticidally active compound of the following formula:



wherein R and R<sup>1</sup> individually are alkyl, alkynyl or alkenyl group containing up to 6 carbon atoms, R<sup>2</sup> is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R<sup>3</sup> is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur, wherein said insecticidal active compound is Acephate;

- (ii) 0.1-5.0% w/w a dispersing agent;
- (iii) 0.1-3% w/w a wetting agent;
- (iv) 0.01-0.08% w/w an antifoaming agent;

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(v) 0.01-1% w/w a stabilizer and

(vi) fillers to make 100%,

wherein said granule has a length of 1.5-3.0 mm and a diameter of 0.5-1.5 mm.

2. The chemically stable phosphoramidothioate granule of claim 1, wherein said dispersing agent is a derivative of sulphonated fatty alcohol.

3. The chemically stable phosphoramidothioate granule of claim 1, wherein said wetting agent is selected from the group consisting of calcium and sodium salt of alkylaryl sulphonate.

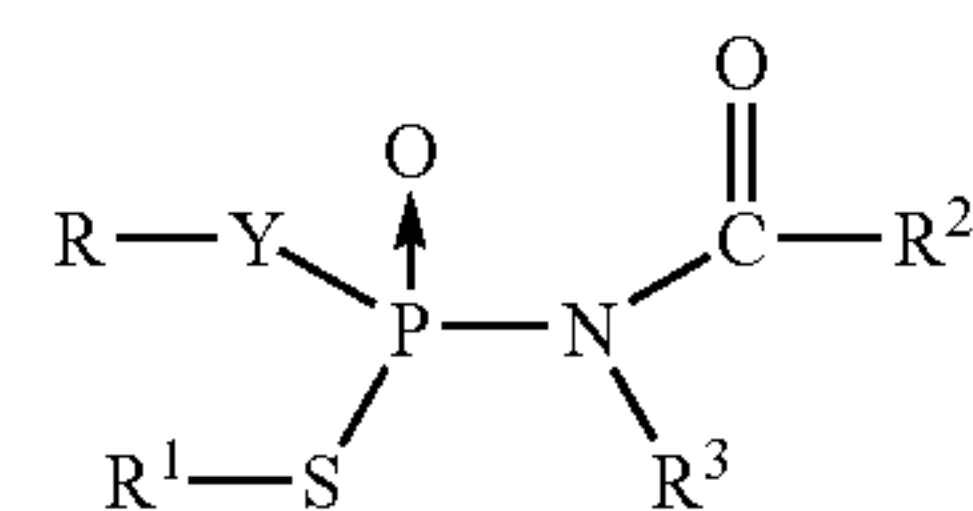
4. The chemically stable phosphoramidothioate granule of claim 1, wherein said antifoaming agent is a silicon oil defoamer.

5. The chemically stable phosphoramidothioate granule of claim 1, wherein said stabilizer is a salt of higher fatty acid.

6. The chemically stable phosphoramidothioate granule of claim 1, wherein said stabilizer is a salt of higher fatty acid.

7. A chemically stable dry flow, low compact, dust free soluble phosphoramidothioate granule consisting of

(i) 85-98% w/w an insecticidally active compound of the following formula:



wherein R and R<sup>1</sup> individually are alkyl, alkynyl or alkenyl group containing up to 6 carbon atoms, R<sup>2</sup> is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R<sup>3</sup> is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur, wherein said insecticidal active compound is Acephate;

- (ii) 0.1-5.0% w/w a dispersing agent;
- (iii) 0.1-3% w/w a wetting agent;
- (iv) 0.1-3% w/w a binding agent;
- (v) 0.01-0.08% w/w an antifoaming agent;
- (vi) 0.01-10% w/w a disintegrating agent;
- (vii) 0.01-1% w/w a stabilizer and
- (viii) fillers to make 100%,

wherein said granule has a length of 1.5-3.0 mm and a diameter of 0.5-1.5 mm.

8. The chemically stable phosphoramidothioate granule of claim 7, wherein said dispersing agent is a derivative of sulphonated fatty alcohol.

9. The chemically stable phosphoramidothioate granule of claim 7, wherein said wetting agent is selected from the group consisting of calcium and sodium salt of alkylaryl sulphonate.

10. The chemically stable phosphoramidothioate granule of claim 7, wherein said binding agent is selected from the group consisting of sucrose and starch derivatives and a blend thereof.

11. The chemically stable phosphoramidothioate granule of claim 7, wherein said antifoaming agent is a silicon oil defoamer.

12. The chemically stable phosphoramidothioate granule of claim 7, wherein said disintegrating agent is swelling type clay selected from the group consisting of bentonite and zeolite.

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(12) **INTER PARTES REVIEW CERTIFICATE** (3329th)

**United States Patent**  
**Jadhav et al.**

(10) **Number:** **US 7,473,685 K1**  
(45) **Certificate Issued:** **Nov. 29, 2023**

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(54) **PROCESS FOR PREPARATION OF  
CHEMICALLY STABLE, DRY-FLOW, LOW  
COMPACT, DUST FREE, SOLUBLE  
GRANULES OF  
PHOSPHOROAMIDOTHIOATES**

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(73) **Assignee: UPL NA INC.**

**Trial Number:**

IPR2020-01113 filed Jun. 17, 2020

**Inter Partes Review Certificate for:**

Patent No.: **7,473,685**  
Issued: **Jan. 6, 2009**  
Appl. No.: **11/060,283**  
Filed: **Feb. 18, 2005**

The results of IPR2020-01113 are reflected in this inter partes review certificate under 35 U.S.C. 318(b).



**INTER PARTES REVIEW CERTIFICATE**  
**U.S. Patent 7,473,685 K1**  
**Trial No. IPR2020-01113**  
**Certificate Issued Nov. 29, 2023**

**1**

**2**

AS A RESULT OF THE INTER PARTES  
REVIEW PROCEEDING, IT HAS BEEN  
DETERMINED THAT:

Claims 7-12 are found patentable.

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Claims 1-4 are cancelled.

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